KFKI-71-23

M. Roder

ON THE RADIOLYSIS OF HYDROCARBON MIXTURES

Hungarian Academy of Sciences

CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS

BUDAPEST

KFKI-71-23

ON THE RADIOLYSIS OF HYDROCARBON MIXTURES

M. Roder

Central Research Institute for Physics, Budapest, Hungary
Chemistry Department

Presented at the Third Tihany Symposium on
Radiation Chemistry, May 10th - 15th, 1971
Hungary

In the radiolysis of binary mixtures of organic liquids it has often been found that there is either an enhanced or reduced decomposition of one component due to the presence of the other. These observed decreases or increases are in excess of those expected from the mixture law. Since the energy of ionizing radiation is absorbed in multi-component systems proportionally to the electron fraction of the components /mixture law/, the deviation from additivity can be due to physical interactions /energy and charge transfer/ and chemical interaction involving the making and breaking of chemical bonds /radical scavenging/.

Although the nature of both types of interaction has been extensively investigated and discussed, especially for cyclohexane - benzene mixtures [1] , their relative importance is farfrom being resolved. The purpose of the present investigation was to attempt to determine the relative contribution of these various interactions for three different mixtures: namely, cyclohexane - hexamethylbenzene /HMB/, benzene-HMB, and toluene - HMB. The studies were confined to liquid systems and to the determination of the main gaseous products of radiolysis /hydrogen and methane/ and their yields.

EXPERIMENTAL

Hexamethylbenzene /"Fluka" reagent grade/ was purified by recrystallization in ethanol and further threefold sublimation under vacuum. Gas chromatographic analysis of the repurified HMB revealed less than 0.07 % of impurities. Cyclohexane /"Merck" spectroscopic grade/ was purified by passage through silica gel, Benzene and toluene /"Reanal" reagent grade/ were shaken with cc. H_2SO_4, then washed with water and shaken with 10 % $NaHCO_3$ solution, washed again with water and dried with $CaCl_2$ and metallic Na. This was fol-

lowed by distillation at atmospheric pressure in a 25 - theoretical - plate column. The middle fraction of the distillate was retained; gas chromatographic analysis showed it contained no impurities. The purified solvents were degassed and distilled under vacuum in greaseless systems and stored in evacuated storage vessels fitted with break seals until used.

Solutions of low HMB concentration were prepared in bulk and aliquots were placed into irradiation vessels fitted with break seals which were degassed by the freeze - thaw method on a vacuum line and sealed. Blank runs in which the reaction mixtures were not irradiated were carried out to determine any loss of solute during the degassing procedure. Solutions of higher HMB concentrations were made up by weight. The HMB was weighed in the irradiation cell, which was then sealed to the vacuum line; after evacuation of the cell a storage vessel of liquid solvent was attached to the vacuum line, its seal was broken off and a known quantity of solvent was distilled into the cell and sealed off. Irradiation was performed with a Co^{60} gamma ray source. Dose rate was measured with a Fricke dosimeter, taking G/III/ - 15.6 and allowing for the different electron densities of the dosimeter and the investigated systems. Temperatures above the ambient temperature were regulated by a furnace to $\pm$ 2°C.

After irradiation the sample vessels were sealed onto a vacuum system combined with a Toepler pump and the gaseous product fraction volatile at -196°C was measured with a McLeod gauge. The collected gaseous fraction was analysed by gas chromatography. Individual yields were determined by calibration of the detector.

HMB is a crystalline compound with a melting point at 166°C. Since its solubility in the investigated solvents is low at the ambient temperature, irradiations were performed at 20 - 170°C. Heat treatment at 180°C over 30 hours did not show any decomposition of investigated compounds, which means that formation of products below this temperature in these experiments is due solel to radiolytic effects.

RESULTS AND DISCUSSION

Aliphatic- aromatic mixture

The radiolysis of the fully methyl substituted symmetrical benzene derivative hexamethylbenzene has already been studied in detail [2]. Table I shows the yields of products obtained from HMB during radiolysis in the liquid phase at 170°C. That the aromatic character of HMB is as strong as in other alkyl - benzenes is shown by the value of its decomposition yield - 2.16 molecules/100 eV. The corresponding value for benzene is about I molecule/100 eV |3|, that for isopropylbenzene 1.8 molecule/100 eV [4], and that for liquid aliphatic hydrocarbons 6-8 molecules/100 eV [5]. Although all the H_2 formed during HMB radiolysis derives from the aliphatic part of molecule its yield is about 10 times smaller than that from pure aliphatic molecules, which indicates that a very powerful protective effect is exerted by the aromatic ring.

However, unlike with other aromatic hydrocarbons, where the total gas yield represents only 4- 12 % of the total decomposition yield, practically all the decomposition of HMB can be accounted for by the formation of gaseous products if the yields and modes of their formation are considered. This means that in the case of HMB the addition of an H atom to the aromatic ring of the molecule is an unimportant process. It is likely that because of the presence of six methyl groups the steric hindrance may be so strong as to prevent completely hydrogen addition. This conclusion is supported by the failure of ESR measurements to demonstrate the presence of "dienyl" type radicals; such radicals could be produced only by H atom addition. The absence of H atom addition reaction in HMB should be of interest in the understanding of the intermolecular protective effect of aromatic compounds. The significant feature of investigations on aliphatic hydrocarbon - HMB mixtures is the absence from the mixtures of compounds which could scavenge H atoms, which means that if protective effects are found to take place, those mechanisms based on radical scavenging can be ignored.

Table I

Product yields from the radiolysis of hexamethylbenzene at 170°C

Product	G value
Hydrogen	0.442
Methane	0.661
Ethane	0.0045
Propane	0.0002
Pentamethylbenzene	0.35
Polymer	0.154
Disappeared Hexamethylbenzene /-HMB/	2.16

Fig. 1 displays the observed hydrogen and methane yields from cyclohexane - HMB mixtures irradiated at 170°C plotted as functions of the electron fraction of HMB over the full range of composition. Since the $G/H_2/$ for the pure cyclohexane decreases with increasing dose, each sample was irradiated with the same dose of 1.7×10^{20} eV.g^{-1}. The dashed lines in Fig. 1 represent the yields of hydrogen and methane that would be expected if each component of the mixture were unaffected by the presence of the other; for hydrogen /and correspondingly for methane/ the line fits the relationship

$$G/H_2/_{exp.} = \varepsilon_{C_6H_{12}} G/H_2/^{\circ}_{C_6H_{12}} + \varepsilon_{C_6/CH_3/_6} G/H_2/^{\circ}_{C_6/CH_3/_6}$$

where $G/H_2/^{\circ}_{C_6H_{12}}$ and $G/H_2/^{\circ}_{C_6/CH_3/_6}$ are the hydrogen yields for pure cyclohexane and pure HMB, respectively, and $\varepsilon_{C_6H_{12}}$ and $\varepsilon_{C_6/CH_3/_6}$ are the electron fractions of the respective components. From Fig. 1, in which each point is the average of three measurements, it can be seen that in no case does the yield correspond to that expected from the electron fraction of the individual components. At low HMB concentrations the observed $G/H_2/$

falls off very rapidly, but at high concentrations the effect of HMB shows less tendency to decrease the hydrogen yield; a similar phenomena has been observed in cyclohexane - benzene mixtures. The observed $G/CH_4/$ exhibits a positive deviation from the mixture law and this deviation is especially significant in mixtures with a small HMB concentration.

In Fig. 2 the radiolytic hydrogen yield is plotted as a function of HMB concentration in cyclohexane for samples irradiated at 70°C. The temperature dependence of $G/H_2/$ was checked for the 10^{-2} - 10^{-1} M concentration solutions and was found to be unchanged from 20°C to 70°C. Results obtained by Stone and Dyne [6] for cylohexane-benzene mixtures are also presented in the figure; these data are consistent with the results of Burton [7], Freeman [8] and Klots [9]. The plots show that the effect of HMB on the $G/H_2/$ is very similar to that observed for the cyclohexane-benzene solutions.

From the above figures one can conclude that cyclohexane decomposition is reduced because of a protective effect of HMB ; this is roughly the same magnitude as that exerted by benzene. From the fact that the observed $G/CH_4/$ is greater than the $G/CH_4/_{exp}$ over the whole range of compositions, it follows that the effect of HMB on cyclohexane is a sacrificial type of protection, i.e. in consequence of the interaction the decomposition of HMB is sensitized.

It has been mentioned above that in the radiolysis of HMB the addition reaction to the aromatic ring is absent, and thus the cyclohexane - HMB system is one of the few cases where one can positively say that the fate of intermediate radicals is not affected to some extent by the presence of the protecting compound. This means firstly that the chemical type of interaction can take no part in the protection effect. Assuming that preferential activation of a solute of small concentration in the solution is not expected, it also means that the deviation from additivity has to be attributed solely to characteristic effects during the electronic relaxation stages. The values of the ionization potentials /9.88 eV for cyclohexane [10] and 7.85 eV for HMB |11|/ and the known electronic excitation states /∿7 eV for cyclohexane

[12] and ∿4 eV for HMB [13]/ are such that a protective effect exerted by HMB on cyclohexane through transmission of energy in the form of electronic excitation and through transfer of electric charge is feasible. There are numerous data indicating the comparatively important role of ionic states in the radiolysis of cyclohexane [1]. Asmus et al.[14], on the basis of experiments with different kind of scavengers, evaluated the $G/H_2/$ coming from ionic processes as 3.9, against a contribution of 1.77 from non-ionic processes. From their nanosecond pulse radiolysis studies on cyclohexane Thomas et al. [5] likewise concluded that the ionic species was more significant. It can be concluded that in the protecting effect of HMB for cyclohexane charge transfer interaction plays a greater role than excitation transfer. From the present investigation, however, it is difficult to establish the relative probability of the two processes.

Aromatic mixtures

Benzene and toluene where chosen for the investigations on the effect of HMB on aromatic hydrocarbons. These compounds have many spectral features in common with HMB, as indicated by their polarizabilities and known absorption and luminescence spectra [13,16,17,18] , but they differ substantially in the values of ionization potentials /7.85 eV for HMB, 9.24 eV for benzene and 8.82 eV for toluene [10]/. The hydrogen and methane yields from the benzene - HMB and toluene - HMB mixtures irradiated with a dose of 1.5×10^{21} eV.g^{-1} are plotted as functions of the HMB electron fraction in Figs. 3 and 4, respectively. It can be seen that in both cases the values of $G/H_2/$ and $G/CH_4/$ are approximately linear functions of the electron fraction of HMB. This behaviour is observed even though the differences in ionization potentials of ∿ 1.4 eV for benzene - HMB and ∿ 1.0 eV for toluene - HMB mixtures make charge transfer to HMB possible. From investigations of benzene and toluene by the method of nanosecond pulse radiolysis Cooper et al. |19| concluded that the radiation chemistry of benzene and toluene is similar, and that - unlike with cyclohexane - the excited species play an important role,

in comparison to the ionic species, among the intermediates. Taking these findings into consideration, we would expect that if there are any interactions causing the deviation of yields from additivity in these systems, then excitation energy transfer would be the more important. Since in the systems investigated the components have similar excited state levels, and thus the energy levels are not favorable for an excitation energy transfer, we did not, in fact, observe essential deviation from the mixture law.

The following statements can be made concerning the experimental results obtained up to date:

1/ In spite of the charge transfer to HMB being exothermic by more than 1.0 eV, there are no apparent interactions between benzene and HMB or between toluene and HMB, and thus the radiolysis of their mixtures follows the additivity.

2/ HMB shows a protective effect in cyclohexane decomposition similar to that for benzene towards cyclohexane. This similarity gives additional evidence of the negligibility of the scavenging effect in the protection of aliphatic by aromatic hydrocarbons.

REFERENCES

[1] J. Kroh, Rad. Res. Rev., 1, 411 /1969/ /a review article on the topics/.

[2] M. Roder, Acta Chimica, in press

[3] W.G. Burns, C.R.V. Reed, Trans. Far. Soc., 59, 101 /1963/

[4] R.R. Hentz, J. Phys. Chem., 66, 1622 /1962/

[5] W.E. Falconer, R. Salovey, J. Chem. Phys., 44, 3151 /1966/

[6] J.A. Stone, P.J. Dyne, Rad. Res., 3, 353 /1963/

[7] J.P Manion, M. Burton, J. Phys. Chem., 56, 560 /1952/

[8] G.R. Freeman, J. Chem.Phys., 33, 71 /1960/

[9] C.E. Klots, Y. Raef, R.H. Johnsen, J. Phys. Chem., 68, 2040 /1964/

[10] K. Watanabe, J. Chem. Phys., 26, 542 /1957/

[11] F.I. Vilesov, Zh. Fiz. Khim., 35, 2010 /1961/

[12] R.A. Holroyd, Fundamental Processes in Rad. Chem., 1968 p. 448

[13] I.P. Vinogradov, I.V. Alesin, N.Ja. Dodonova, Optika i Spectroscopia, 29, 477 /1970/ 28, 170 /1970/

[14] K.D. Asmus, J.M. Warman, R.H. Schuler, J. Phys. Chem., 74, 246 /1970/

[15] J.K. Thomas, K. Johnson, T. Klippert, R. Lowers, J. Chem. Phys., 48, 1608 /1968/

[16] S. Stokes, J. Chem. Phys., 39, 2309 /1963/

[17] L.G. Christophorou, R.N. Compton, Health Phys., 13, 1277 /1967/

[18] R.L. Flurry, P.G. Lycos, Mol. Phys., 6, 283 /1963/

[19] R. Cooper, J. K. Thomas, J. Chem. Phys., 48, 5097 /1968/

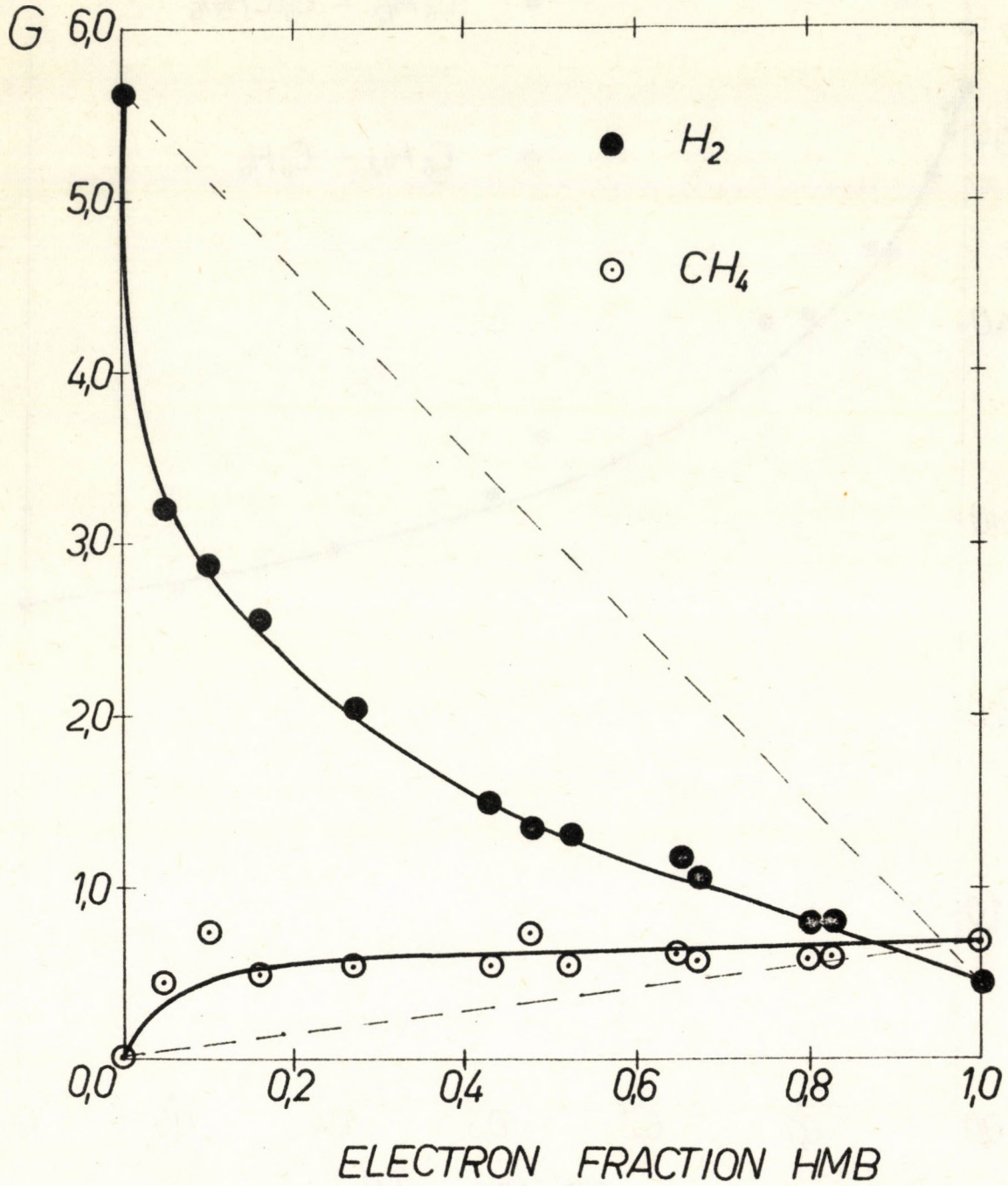


Fig. 1

Dependence of $G/H_2/$ and $G/CH_4/$ on the electron fraction of hexamethylbenzene in cyclohexane-hexamethylbenzene solutions irradiated at 170°C

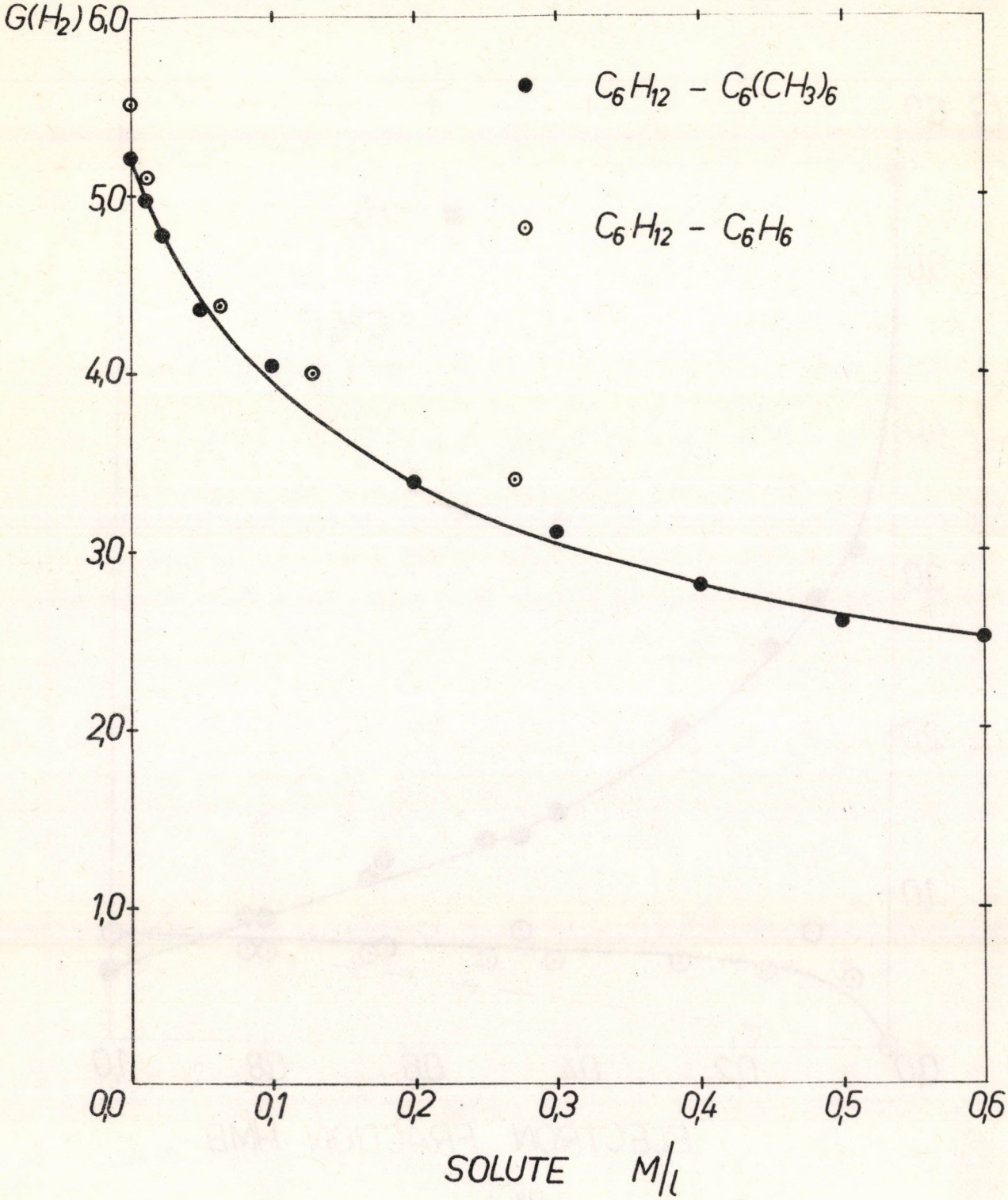


Fig. 2

Dependence of $G/H_2/$ on solute concentration in solutions irradiated at 70°C

● cyclohexane - hexamethylbenzene solutions

⊙ cyclohexane - benzene solutions [6]

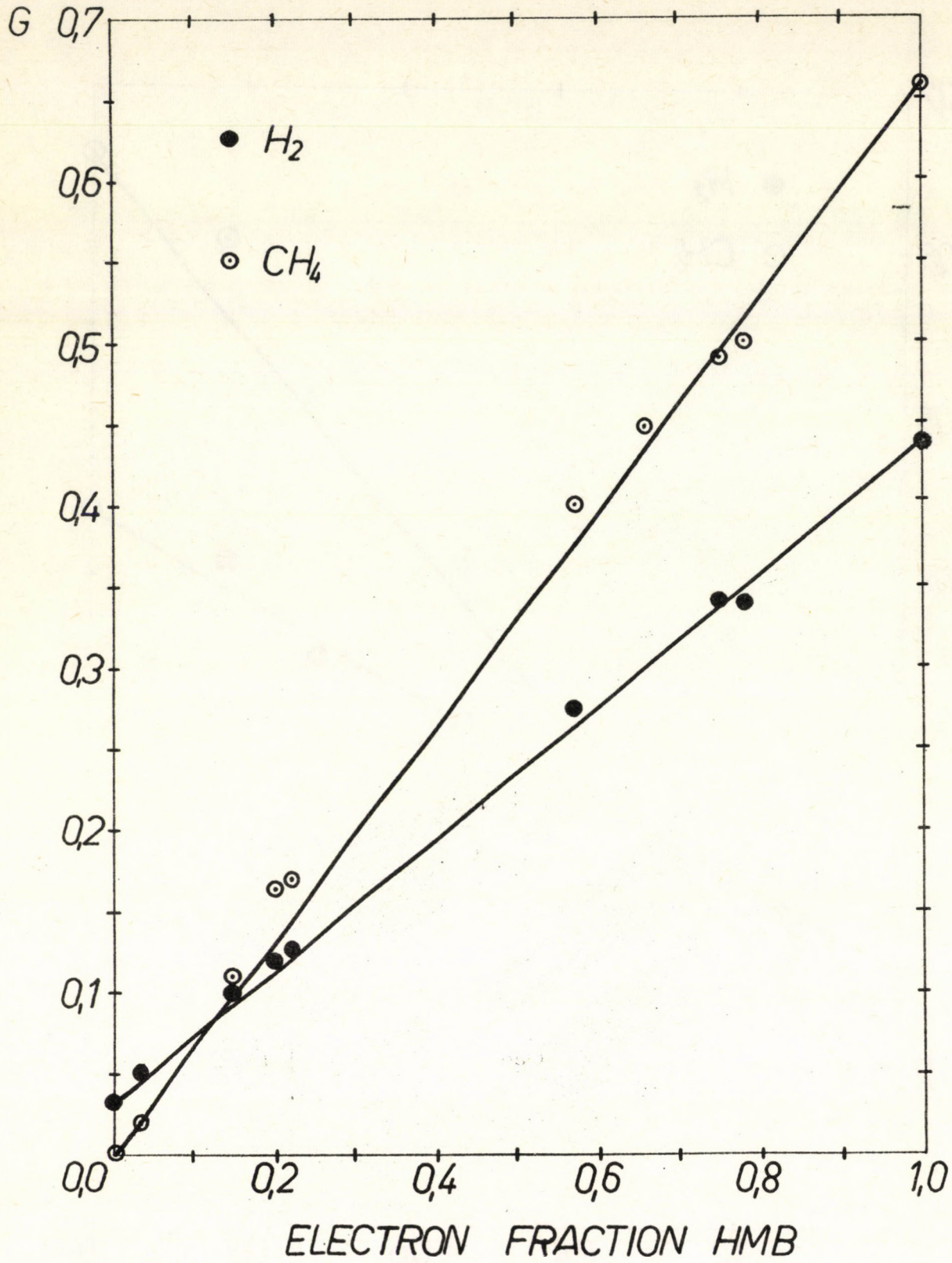


Fig. 3

Dependence of $G/H_2/$ and $G/CH_4/$ on electron fraction of hexamethylbenzene in benzene - - hexamethylbenzene solutions irradiated at 170°C

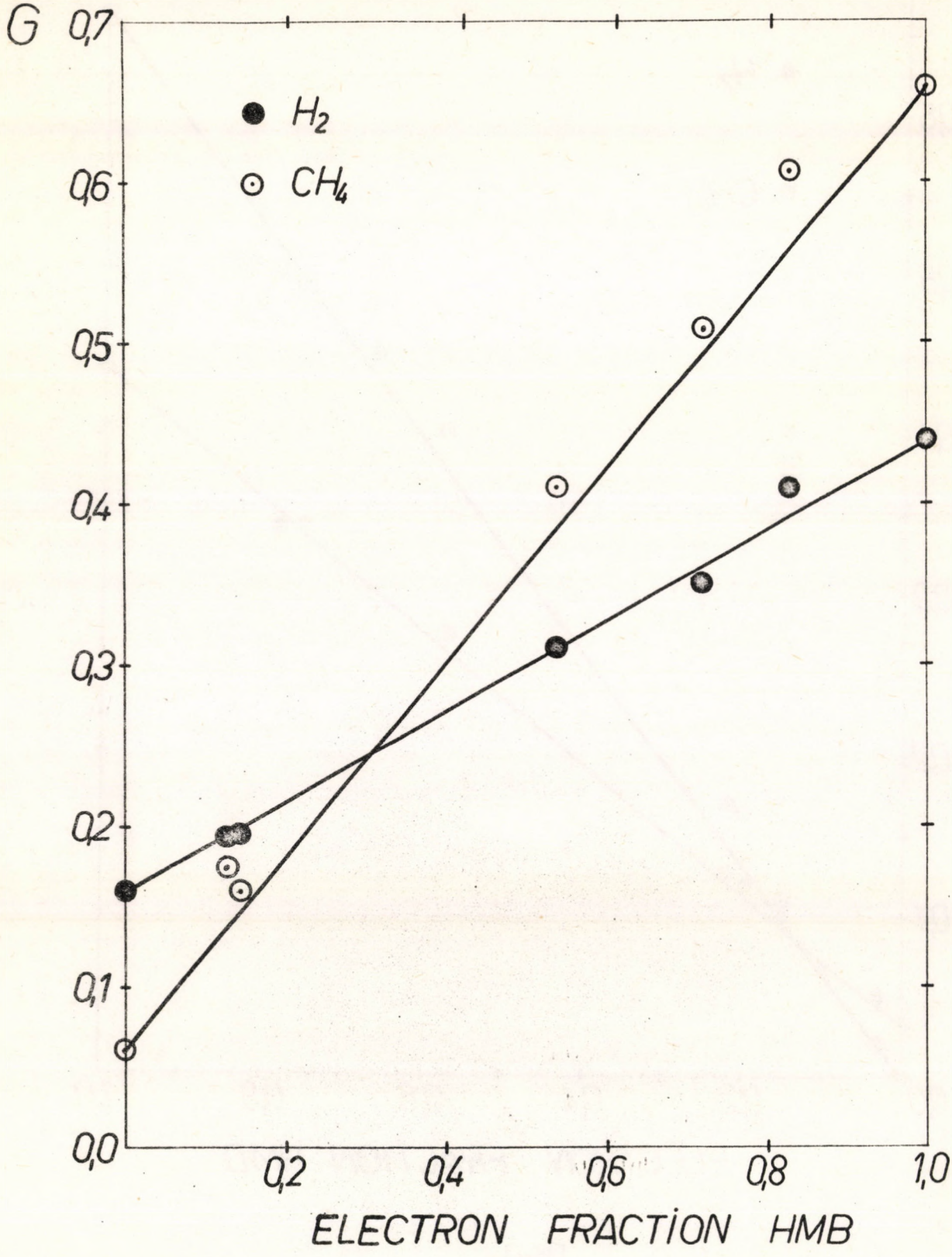
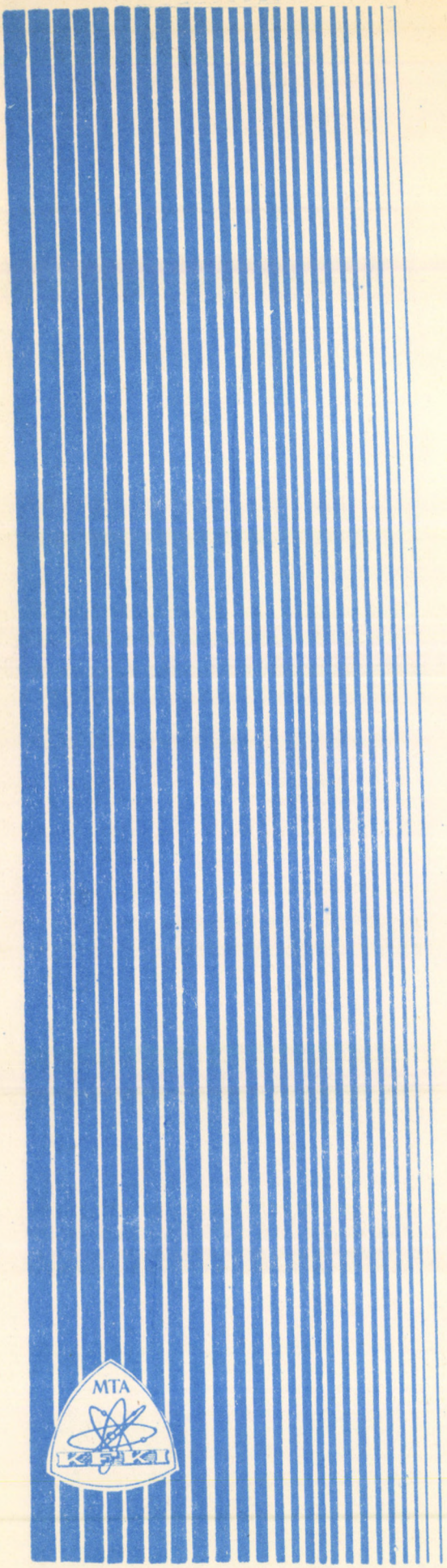


Fig. 4

Dependence of $G/H_2/$ and $G/CH_4/$ on electron fraction of hexamethylbenzene in toluene- - hexamethylbenzene solutions irradiated at 170°C

61. 883



Printed in the Central Research Institute for Physics,
Budapest, Hungary
Kiadja az MTA Központi Fizikai Kutató Intézete
Könyvtár-Kiadói Osztálya
O.v.: Dr. Farkas Istvánné
Szakmai lektor: Schiller Róbert
Nyelvi lektor: Timothy Wilkinson
Példányszám: 430 Törzsszám: 71-5601
Készült a KFKI házi sokszorositójában
F.v.: Gyenes Imre